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Supporting Information:

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Jing Lyu,[†,‡] Yongsheng Gao,[†] Zidan Zhang,[§] Udo Greiser,[†] Piotr Polanowski,[#] Jeremiasz K. Jeszka,[%] Krzysztof Matyjaszewski,[‖] Hongyun Tai[⊥] and Wenxin Wang[*,†,‡]

[†]Charles Institute of Dermatology, School of Medicine, University College Dublin, Belfield, Dublin 4, Ireland

[‡]School of Mechanical and Materials Engineering, University College Dublin, Dublin 4, Ireland

[§]Division of Polymer Chemistry and Materials, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

[#]Department of Molecular Physics, Technical University of Lodz, 90-924, Lodz, Poland

[%]Department of Man-Made Fibres, Technical University of Lodz, 90-924, Lodz, Poland

[‖]Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA

[⊥]School of Chemistry, Bangor University, Deiniol Road, Bangor, Gwynedd, LL57 2UW, UK

E-mail: wenxin.wang@ucd.ie

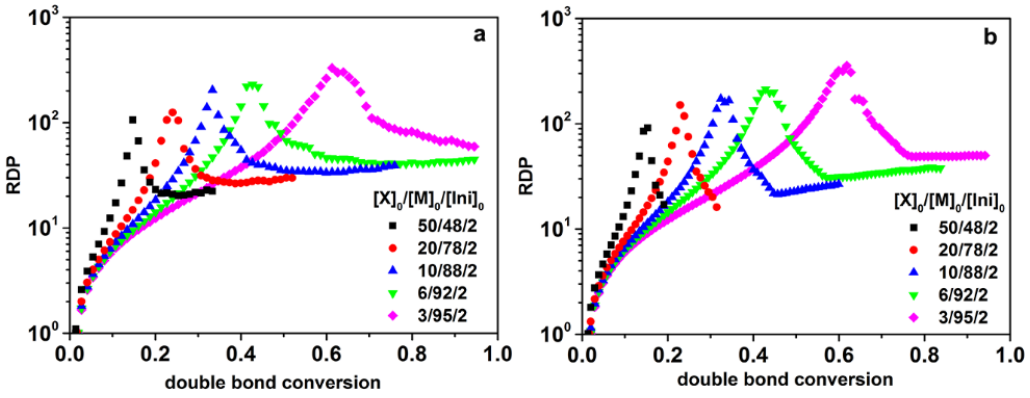

Figure S1. Simulation for ATRcP of monovinyl monomers and divinyl monomers. The dependence of *RDP* plotted vs. double bond conversion, obtained from (a) **w.c.** model and (b) **wo.c.** model for various $[X]_0/[M]_0/[Ini]_0$.

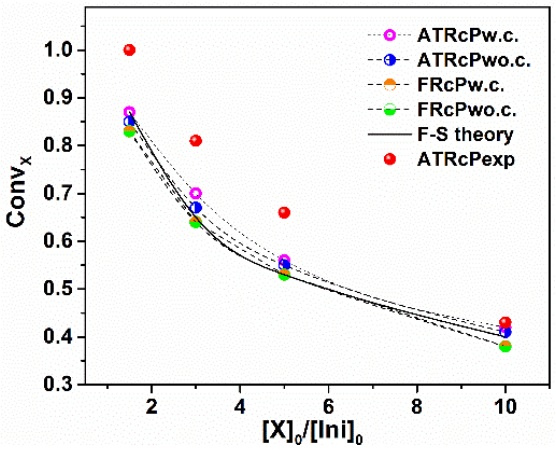

Figure S2. Comparison of the gel points ($Conv_x$) for various initial molar ratios of divinyl monomer to initiator $[X]_0/[Ini]_0$, obtained from ATRcP, FRcP simulations and F-S theory.

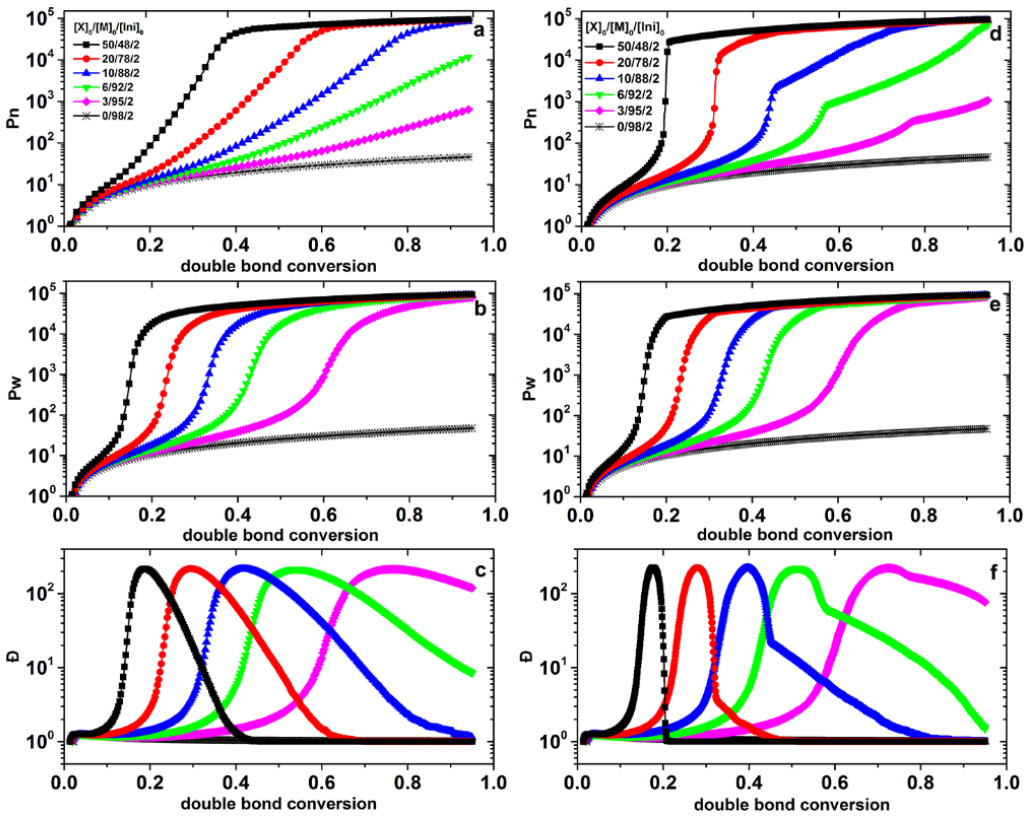

Figure S3. Simulation for ATRcP of monovinyl monomers and divinyl monomers. The growth of P_n with double bond conversion for (a) **w.c.** model and (d) **wo.c.** model. The growth of P_w with double bond conversion for (b) **w.c.** model and (e) **wo.c.** model. The growth of $Đ$ with double bond conversion for (c) **w.c.** model and (f) **wo.c.** model.

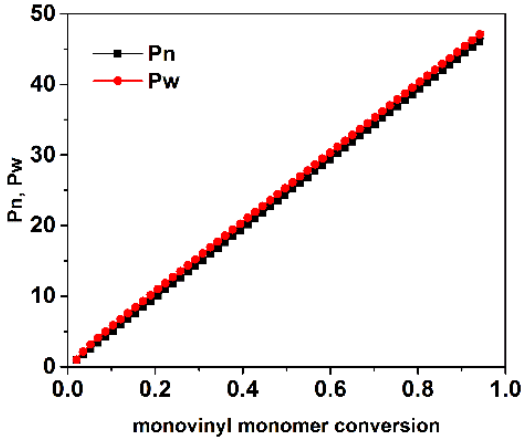

Figure S4. Simulation for ATRP of monovinyl monomers. The linear growth of P_n and P_w with monovinyl monomer conversion.

Table S1. Comparison of gel points of ATRcP of monovinyl and divinyl monomers obtained from experiments, F-S theory and different simulation models.

$[X]_0/[M]_0/[Ini]_0$	**w.c.** sim[a]		**wo.c.** sim[a]		ATRP exp[b]	F-S calc[b]		DLL w.c.[b]		DLL wo.c.[b]	
	$Conv_d$	$Conv_X$	$Conv_d$	$Conv_X$	$Conv_X$	$Conv_d$	$Conv_X$	$Conv_d$	$Conv_X$	$Conv_d$	$Conv_X$
20/78/2	0.24	0.42	0.23	0.41	0.43	0.22	0.40	0.38	0.57	0.34	0.55
10/88/2	0.33	0.56	0.32	0.55	0.66	0.32	0.53	0.50	0.71	0.46	0.68
6/92/2	0.44	0.70	0.43	0.67	0.81	0.41	0.65	0.62	0.83	0.56	0.78
3/95/2	0.64	0.87	0.62	0.85	1.0	0.58	0.82	0.83	0.95	0.76	0.90

[a]The values were calculated in this work. [b]The values for $Conv_x$ were taken from ref. [1,2], and the values for $Conv_d$ were calculated in this work.

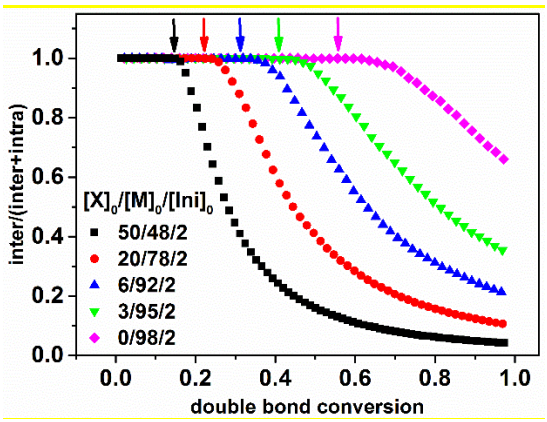

Figure S5. Simulation for ATRcP of monovinyl monomers and divinyl monomers using **w.c.** model shows the ratio of intermolecular crosslinking formed at different conversions. Ratio of intermolecular crosslinks per chain to all crosslinks per chain versus double bond conversion. Arrows indicate gel points.

Reference:

(1) H. Gao, P. Polanowski, K. Matyjaszewski, *Macromolecules* **2009**, *42*, 5925-5932.

(2) P. Polanowski, J. K. Jeszka, K. Krysiak, K. Matyjaszewski, *Polym. (United Kingdom)* **2015**, *79*, 171-178.